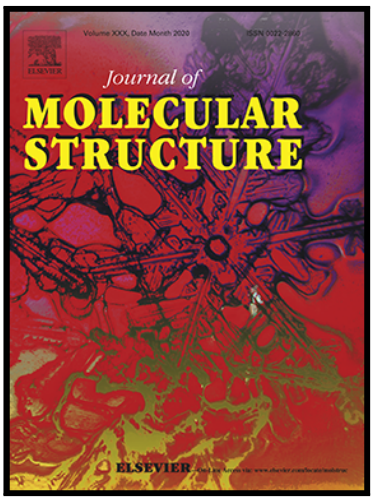

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Novel Sultone Based Brønsted Acidic Ionic Liquids with Perchlorate Counter-Anion for One-pot Synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones

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Abstract

Three novel sultone based Brønsted acidic ionic liquids are introduced. These ionic liquids were prepared in three similar two-steps reactions. The ring opening of 1,4-butane sultone was performed using 1,4-dimethyl piperazine or 1,10-phenantroline as nitrogen nucleophile sources to obtain zwitterions and then followed by acidification by treatment with perchloric acid to give the introduced ionic liquids. FTIR, ^{1}HNMR, ^{13}C-NMR, TGA and CHNS analysis techniques were used for the characterization of these ionic liquids. These ionic liquids are completely water soluble and have good thermal stability. Their catalytic efficiency was checked for the preparation of polycyclic 2*H*-indazolo[2,1-*b*]phthalazine-trione compounds. Small amount (3-7 mmol%) of the prepared acidic ionic liquid catalysts is required and targeted products are obtained in short times (6-25 min) at high yields (86-96%). Moreover, the introduced acidic ionic liquids are completely green, environmental benign and task specific and simply recoverable up to six consecutive runs without significant decrease in their catalytic.

***Keywords*:** Sultone, Brønsted Acidic Ionic Liquid, Task specific, Green Chemistry, Phthalazine-trione

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1. Introduction

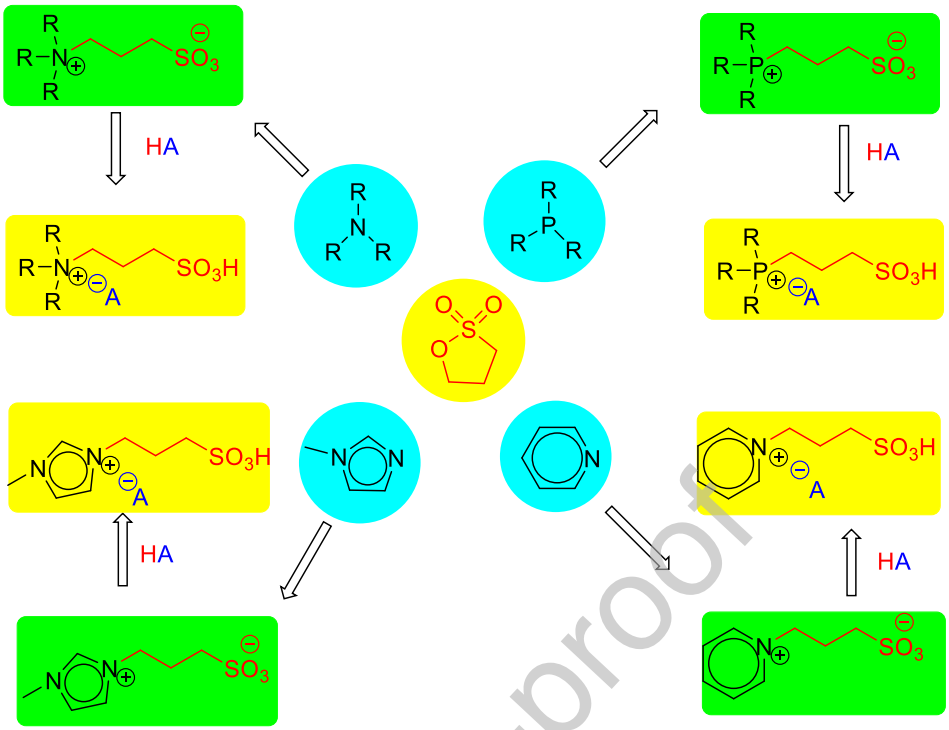
From the academic laboratories to chemical manufacturing plants, Brønsted acids have been extensively used [1]. Solid acids are nonvolatile and environmental benign materials but they suffer from high molecular weight/active-site ratios which rapid deactivation from coking limits their application to some degree. On the other hand, mineral liquid acids have a greater effective surface area and efficient catalysis but they also have some disadvantages such as corroding the equipment, not recoverable/reusable, incomplete separation of this kind of acid catalysts from the final product, the need for the neutralization of the used catalyst increases the economic costs and to some extent are noxious to the environment [2].

Recently, water-stable room-temperature ionic liquids (RTILs) have been introduced as a powerful alternative to traditional molecular organic solvents due to their particular properties, such as low vapor pressure, wide liquid range, and ease of recovery and reuse that make RTILs a greener alternative to volatile organic solvents [3-7]. The term "task-specific IL" refers to the non-solvent applications of the ILs such as catalyst in the organic synthesis [8–12]. Probably, the most significant subcategory of the task-specific ILs (TSILs) is referred to as Brønsted acidic ionic liquids (BAILs). BAILs have both valuable characteristics of solid acids and mineral acids which are designed for replacement with conventional mineral liquid acids, such as sulfuric acid and hydrochloric acid, in chemical processes [13-17].

The first synthesized Brønsted acid functionalized ILs were reported by Cole and used as solvent catalyst in esterification reaction. The prepared BAILs were reused for at least five times without significant loss of activity in the synthesis of ethyl acetate [18]. The introduction of Brønsted acidic functional groups into cationic or anionic parts of the ILs, especially SO_3H-functional groups, has obviously enhanced their acidity and water solubility, and gives great promise for using ILs as green catalysts in many typical acid-catalyzed organic reactions with good catalytic activities [19-21].

Up to date, various SO_3H-functional Brønsted acidic TSILs that bear an alkane sulfonic acid group in an acyclic trialkanylammonium [22], cyclic aromatic [18] or none-aromatic compounds containing nitrogen such as imidazolium [23], pyridinum or n-alkanyl pyrolidinum [24,25] and triphenylphosphinium [26] cations with hydrogen sulfate counter anions have been synthesized and used as TSILs in many organic transformations (Scheme 1).

Recently, we have prepared some new BAILs based on 1,4-dimethyl piperazinium and 1,10-phenantrolinium cations with phosphotungstate anion counterparts as powerful acidic catalysts for the synthesis of 3,3′-diaryloxindoles [27], 2*H*-indazolo[2,1-*b*]phthalazine−triones [28], esterification reaction [29] and selective oxidation of alcohols [30]. In continuation to our attempts for the synthesis of new BAILs, herein we wish to report three novel BAILs based on 1,4-dimethyl piperazinium and 1,10-phenantrolinium cations with perchlorate anion as powerful recyclable and reusable acidic catalysts for the synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones.

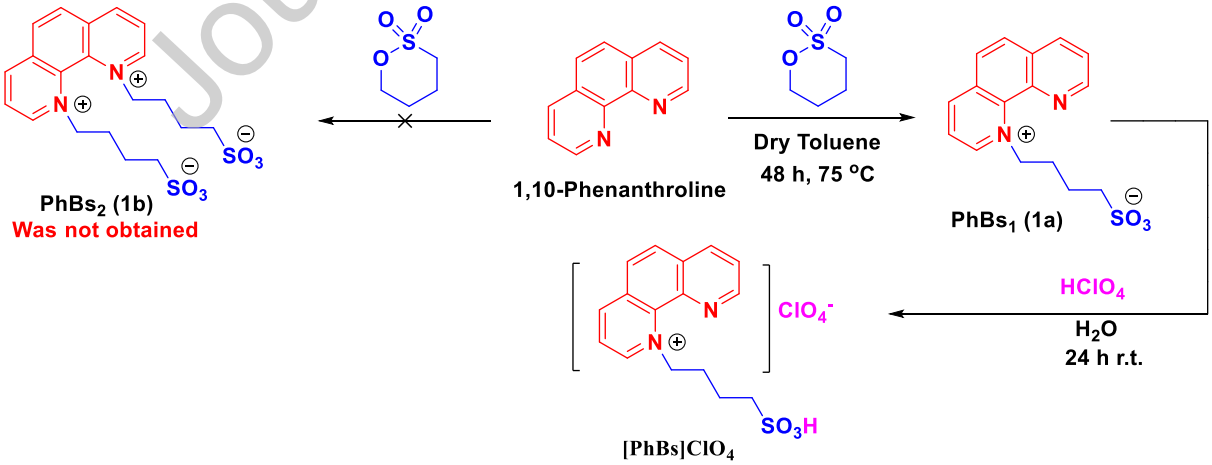


Scheme 1 Synthesis of various BAILs

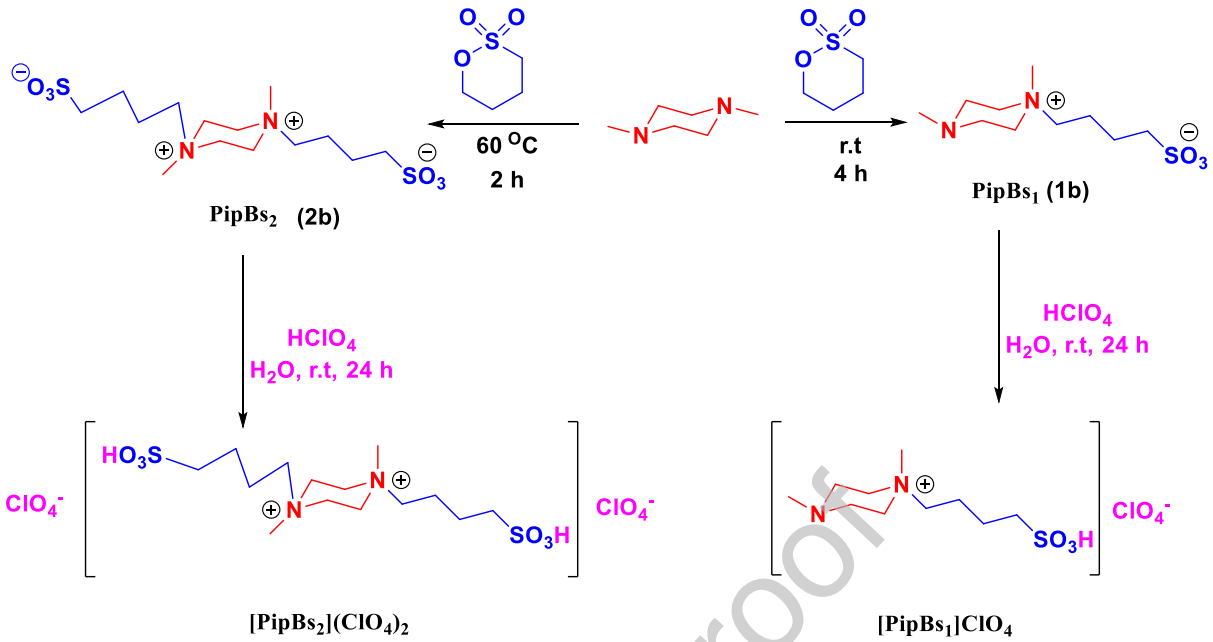
2. Results and Discussion

2.1. Preparation of the introduced BAILs

The schematic routs for the preparation of three novel TSILs have been drawn in schemes 2 and 3. The targeted TSILs were achieved in a two-steps reaction. At the first step, in a S_N2 type reaction, the nitrogen nucleophile from 1,10-phenantroline or 1,4-dimethyl piperazine attacked to C1 of 1,4-butane sultone led to the ring opening of sultone which furnished the phenantrolinium butane sulfonate (2a) or piperazinium butane sulfonate (3a and 3b) zwitterions.



Scheme 2 Preparation of novel $[PhBs_1]ClO_4$ BAIL



Scheme 3 Preparation of novel $[PipBs_1]ClO_4$ and $[PipBs_2](ClO_4)_2$ BAIL

The ^{1}H-NMR spectral analysis of these zwitterions revealed that when 1,10-phenantroline is reacted with 1,4-butane sultone under various molar ratio and thermal conditions, only one of the two nitrogen atoms is attacked and leads to the 1,10-phenantrolinium moiety bearing only one butyl sulfonate branch (See the supplementary). We related this fail to the steric hindrance in double linkers structure and also probably because of the disturbing effect of the enhanced positive charge on the ring aromaticity.

On the other hand, both mono and bis-substituted 1,4-dimethyl piperazinium salts (3a and 3b) were prepared by changing the molar ratios and the reaction temperatures. The mono substituted piperazinium salt was achieved when the equivalent molar ratios of 1,4-dimethyl piperazine and 1,4-butane sultone were reacted at room temperature after 4 h while the bis-substituted piperzinium salt was prepared by the reaction of 1:3 molar ratio of 1,4-dimethyl piperazine and 1,4-butane sultone at 60˚C for 2 h. Next, the completely dissolved phenantrolinium or piperazinium salts in water were reacted with equimolar ratio of $HClO_4$ at room temperature for 24 h. Finally, the evaporation of water solvent gave the targeted BAILs ($[PhBs_1]ClO_4$, $[PipBs_1]ClO_4$ and $[PipBs_2](ClO_4)_2$) (Scheme 4 and Fig. 1).

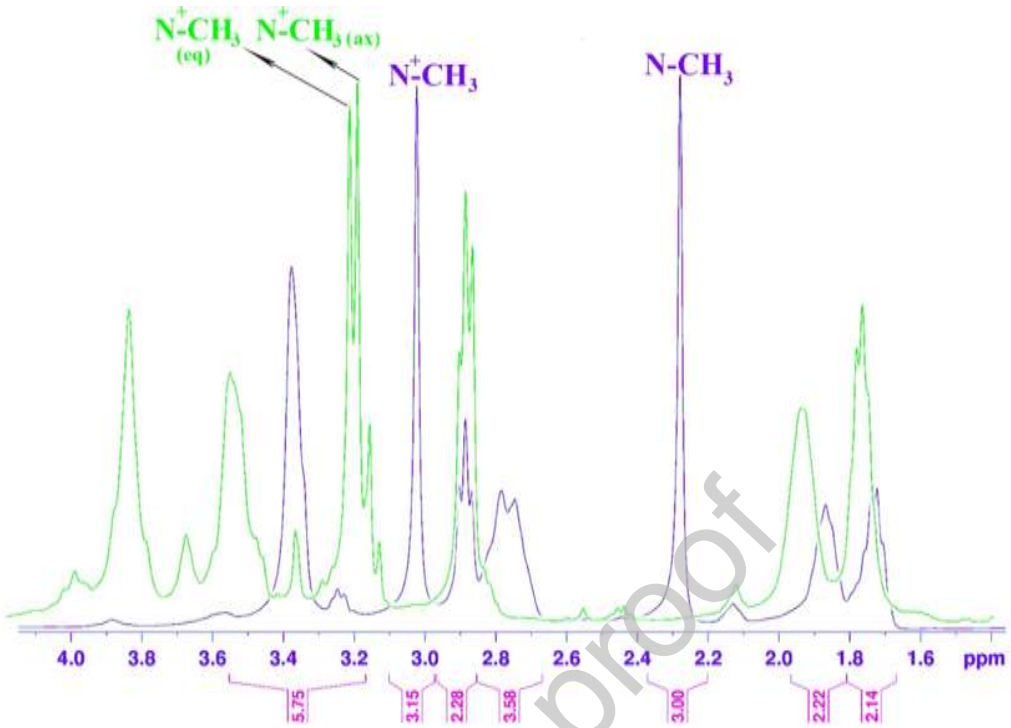
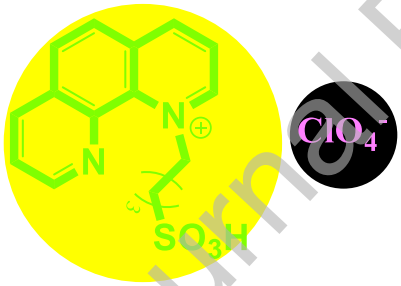
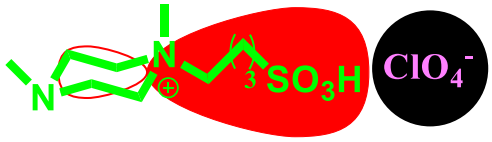


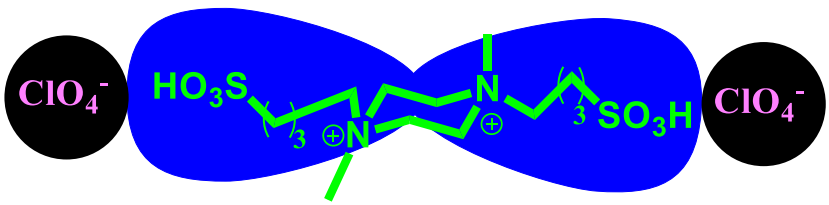
Fig. 1 ^{1}H NMR (400 MHz, D_2O) spectrum of $PipBs_1$ (blue) and $PipBs_2$ (green)



[PhBs1]ClO4



[PipBs1]ClO4



[PipBs2](ClO4)2

Scheme 4 The structural configuration of new introduced BAILs

2.2. FTIR characterization of the prepared novel BAILs

To confirm the successful preparation of these novel BAILs, The FTIR spectra of $[PhBs_1]ClO_4$ and pure 1,10-phenantroline are presented in Fig. 2. The FTIR spectra of $[PipBs_1]ClO_4$ and $[PipBs_2](ClO_4)_2$ with comparative depiction with 1,4-dimetylpiperazine have been shown in Fig. 3. As can be seen in Fig. 2 and 3, in comparison with starting material, the existence of sulfonic acid groups and perchlorate anions has increased the number of vibration modes and has brought completely different FTIR spectra. The FTIR spectrum of $[PhBs_1]ClO_4$ (Fig. 2b), in comparison with the FTIR spectrum of the pure 1,10-phenantroline (Fig. 2a), shows two characteristic absorption bands at 1080 and 1032 cm^{-1} as new peaks which are assigned to the asymmetric ClO_4^- stretching vibration.

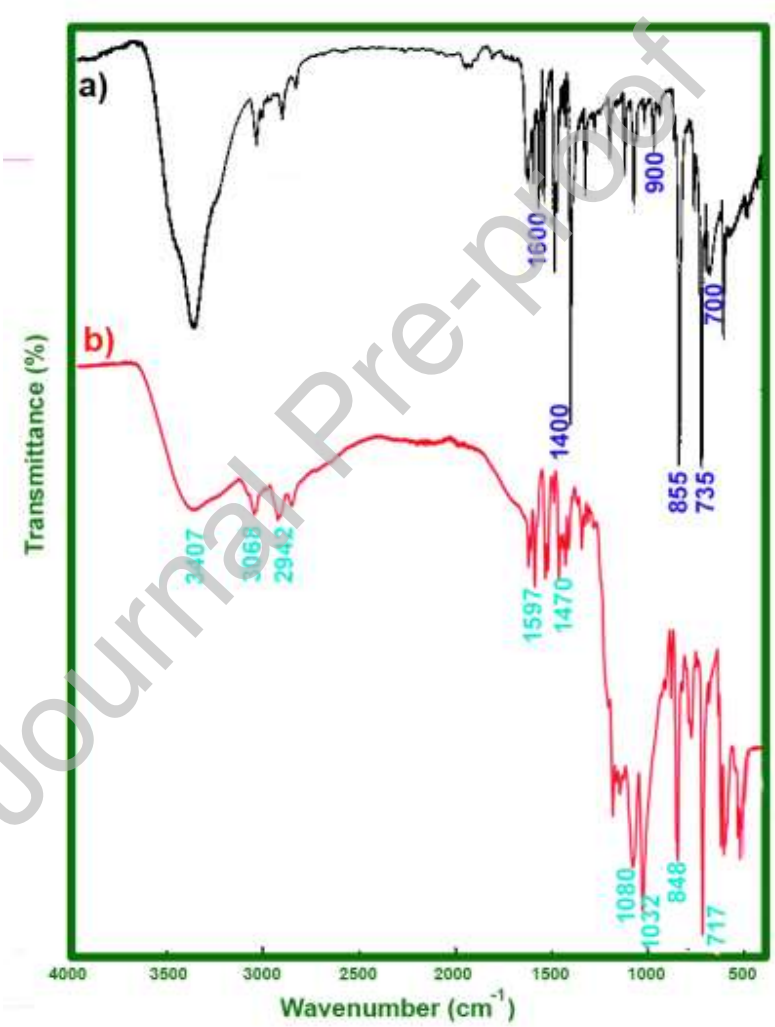


Fig 2 FT-IR spectrum of 1,10-Phenantroline (2a) and $[PhBs_1]ClO_4$ catalyst (2b)

In the case of $[PipBs_1]ClO_4$ these absorption bands are appeared as new bands at 1070 and 1025 cm^{-1} (Fig. 3c *vs* 3a) and for $[PipBs_2](ClO_4)_2$ are appeared at 1073 and 1027 cm^{-1} respectively (Fig. 3b *vs* 3a).

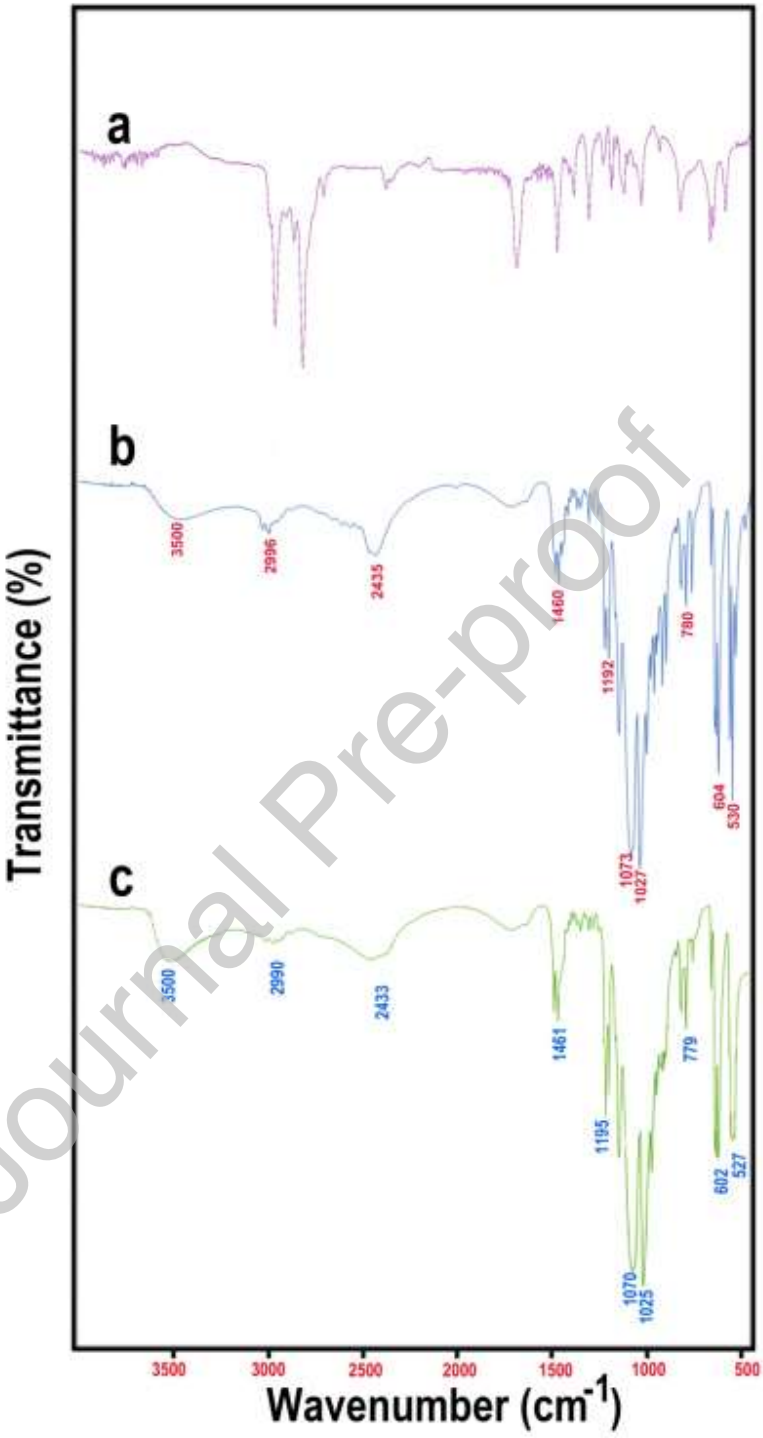


Fig. 3 FT-IR spectrum of 1,4-dimethyl Piperazine (3a), $[PipBs_2](ClO_4)_2$ catalyst (3b) and $[PipBs_1]ClO_4$ (3c)

Furthermore, for all these three prepared BAILs, new bands at nearly 600 cm^{-1} are attributed to symmetric stretching vibration and bands at 530-520 cm^{-1} are referred to bending vibration of ClO_4^- counterpart anion. The broad bands observed at 2900-3500 cm^{-1} in the FT-IR spectra of the BAILs catalysts are referred to OH groups. Finally, the SO_2 asymmetric vibrations of the BAILs are found at around 1470 and 1200 cm^{-1}.

2.3. Study of thermal stability

The thermal stability of the prepared BAILs was investigated by TGA. For all these BAILs as depicted for $[PipBs_2](ClO_4)_2$ in Fig. 3, thermal degradation is started about 200℃, which is acceptable for experimental using. The evaporation of adsorbed water lower than 150℃ is the reason for the slight weight loss at this temperature rang.

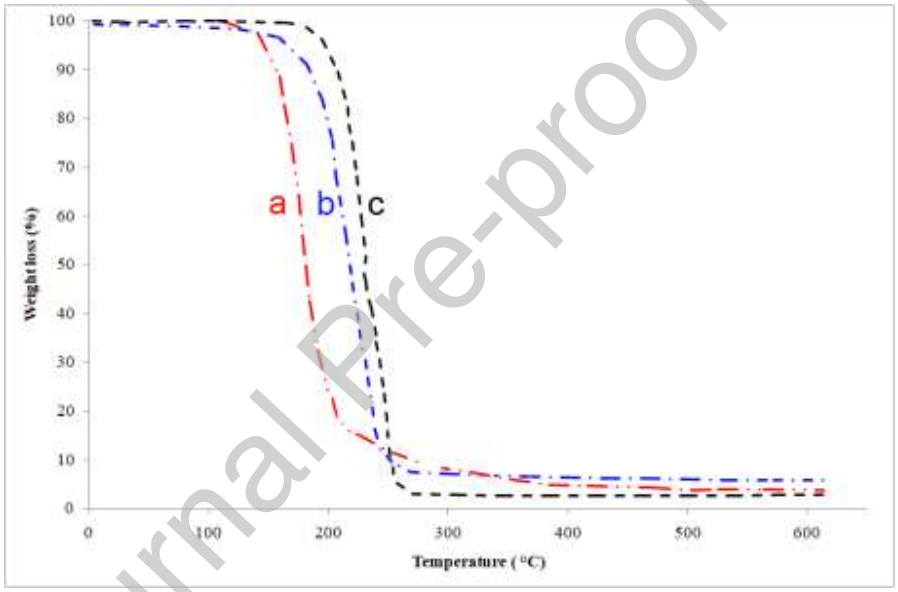


Fig 4 TGA of $[PhBs_1]ClO_4$(4a), $[PipBs_2](ClO_4)_2$ (4b) and $[PipBs_1]ClO_4$ (4c)

2.4. Acidities of the prepared BAILs

Hammet equation was used to evaluate the acidity of the introduced BAILs. The Brønsted acidities of the BAILs were measured using the Hammett method and UV–vis spectroscopy at 110◦C. The Hammett function (H_0) is defined as:

$$H_0 = pK(I)_{aq} + \log([I]/[IH^+])$$

where $pK(I)_{aq}$ is the p*K*a value of the indicator referred to an aqueous solution, IH^+ is the protonated form of indicator, and [I] and $[IH^+]$ are the molar concentrations of unprotonated and protonated form of indicator in the BAILs, respectively (Fig. 5). Moreover, 2,4-dichloro-6-nitroaniline ($pK(I)_{aq} = -3.31$) was

chosen as indicator base (I). The H_0 value of BAILs was calculated by determination of the [I]/[IH^+] ratio from the measured absorbance.

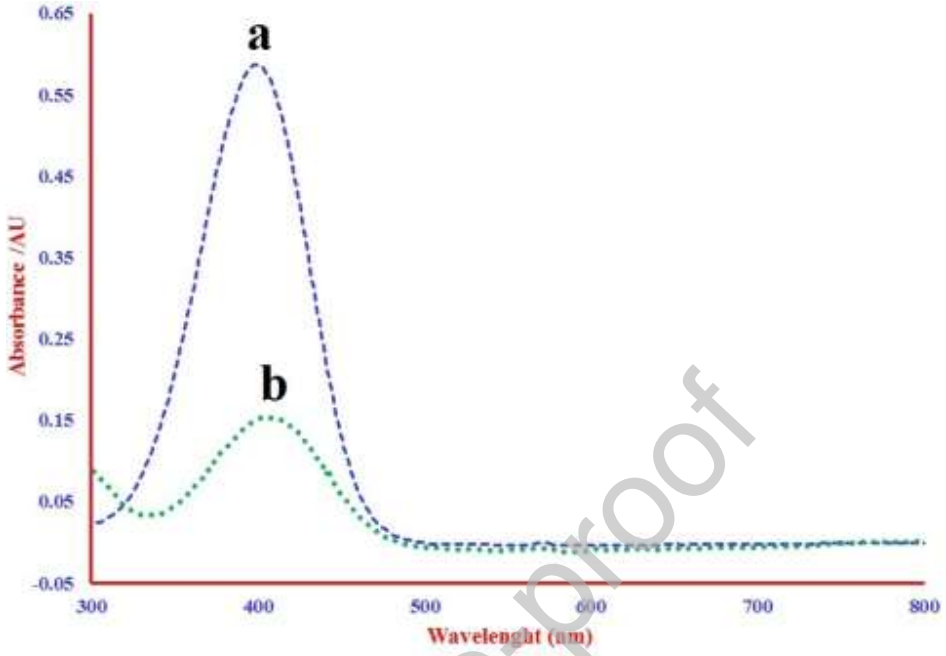


Fig. 5 Absorption spectra of 0.025 mg/ml 2,4-dichloro-6-nitroaniline in ethanol (a) and $[PipBs_2](ClO_4)_2$ (b)

Table 1 H_0 values of the BAILs at 110℃

BAIL	[I] (%)	[HI^+] (%)	H_0
$[PipBs_2](ClO_4)_2$	32	68	-3.64
$[PipBs_1]ClO_4$	40	60	-3.47
$[PhBs_1]ClO_4$	45	55	-3.40

Table 1 shows that $[PipBs_2](ClO_4)_2$ has slightly stronger acidity that $[PipBs_1]ClO_4$ and $[PhBs_1]ClO_4$ is the weakest acid among these BAILs.

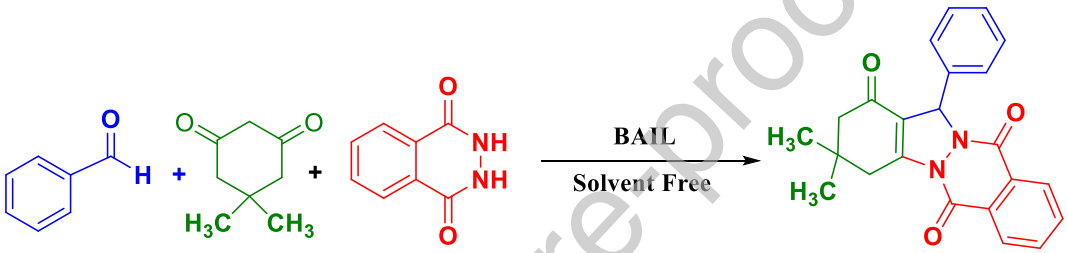
2.5. One-pot synthesis and three-component of 2*H*-indazolo[2,1-*b*]phthalazine-trione derivatives using the introduced BAILs

Using the novel synthesized BAILs in hand, the three-component condensation reaction of aromatic aldehydes, dimedone (and or 1,3-cyclohexanedione), and phthalhydrazide was investigated to study the catalytic activity of the introduced catalysts. At the first, the reaction of benzaldehyde, dimedone, and phthalhydrazide was selected as a model. In order to provide greener procedure, the solvent-free was selected as media condition of choice. The progress of the reaction using various amounts of the three

synthesized [PhBs]ClO_4, [$PipBs_1$]ClO_4 and [$PipBs_2$]$(ClO_4)_2$ as catalysts at different thermal conditions was checked by TLC.

The results with respect to the amount of used catalysts, temperature, reaction times and yields of the product are summarized in table 2. It was found that the best thermal conditions is 110℃ and [$PhBs_1$]ClO_4 or [$PipBs_2$]$(ClO_4)_2$ gave better results than [$PipBs_1$]ClO_4. Moreover, [$PipBs_2$]$(ClO_4)_2$ as catalyst showed slightly more efficiency than [PhBs]ClO_4. However, all three catalysts, in comparison with previously reported catalysts, showed comparative or even superior activity in most cases. The optimized used amount of [$PipBs_2$]$(ClO_4)_2$ was 20 mg (3 mmol%, table 2, entry12), [$PipBs_1$]ClO_4 = 25 mg (7 mmol%, table 2, entry 6) and [$PhBs_1$]ClO_4 = 30 mg (7 mmol%, table 2, entry 9).

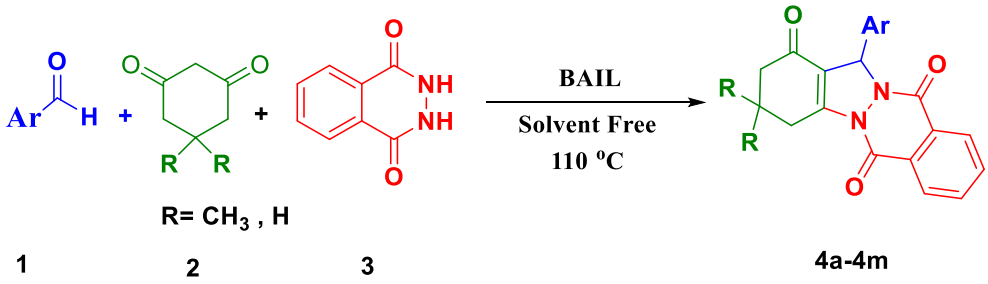
Table 2 Optimization of the reaction conditions for the BAILs catalyzed 2*H*-indazolo[2,1-*b*]phthalazine-triones preparation



Entry	BAIL/ mg	T (℃)	Time(min)	Yield (%)[a]
1	-	r.t	240	-
2	[$PipBs_1$]ClO_4/ 10 mg (3 mmol%)	r.t	240	30
3	[$PipBs_1$]ClO_4/ 20 mg (6 mmol%)	r.t	240	50
4	[$PipBs_1$]ClO_4/ 25 mg (7 mmol%)	r.t	240	60
5	[$PipBs_1$]ClO_4/ 25 mg (7 mmol%)	80	60	75
6	**[$PipBs_1$]ClO_4/ 25 mg (7 mmol%)**	**110**	**20**	**80**
7	[$PhBs_1$]ClO_4 / 20 mg (5 mmol%)	80	60	85
8	[$PhBs_1$]ClO_4 / 30 mg (7 mmol%)	110	20	80
9	**[$PhBs_1$]ClO_4 / 30 mg (7 mmol%)**	**110**	**20**	**92**
10	[$PipBs_2$]$(ClO_4)_2$/ 10 mg (1.5 mmol%)	80	60	75
11	[$PipBs_2$]$(ClO_4)_2$/ 15 mg (2 mmol%)	110	20	85
12	**[$PipBs_2$]$(ClO_4)_2$/ 20 mg (3 mmol%)**	**110**	**10**	**95**
13	[$PipBs_2$]$(ClO_4)_2$/ 25 mg (4 mmol%)	110	10	95

[a] Isolated Yield

After finding the optimum thermal condition and the best used amount of the BAIL catalysts, the generality of the procedure and catalytic role applicability of the introduced BAILs were investigated and the reaction was extended by using various substituted benzaldehydes under optimized condition (Scheme 5 and Table 3).



BAIL=$[PipBs_2](ClO_4)_2$, $[PipBs_1]ClO_4$ **and** $[PhBs_1]ClO_4$

Scheme 5 Synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones catalyzed by introduced BAILs

Table 3 BAILs catalyzed the preparation of 2*H*-indazolo[2,1-*b*]phthalazine-triones

Product	Ar	R	Time(min)	Yield(%)[a]	BAIL Catalyst
4a	C_6H_5	CH_3	10	95	$[PipBs_2](ClO_4)_2$
4b	4-Me-C_6H_4	CH_3	15	92	$[PipBs_2](ClO_4)_2$
4c	4-F-C_6H_4	CH_3	8	89	$[PipBs_2](ClO_4)_2$
4c	4-F-C_6H_4	CH_3	12	93	$[PhBs]ClO_4$
4c	4-F-C_6H_4	CH_3	15	87	$[PipBs_1]ClO_4$
4d	2-Cl-C_6H_4	CH_3	15	91	$[PipBs_2](ClO_4)_2$
4d	2-Cl-C_6H_4	CH_3	20	89	$[PipBs_1]ClO_4$
4e	4-Cl-C_6H_4	CH_3	10	90	$[PhBs]ClO_4$
4e	4-Cl-C_6H_4	CH_3	10	88	$[PipBs_1]ClO_4$
4e	4-Cl-C_6H_4	CH_3	7	94	$[PipBs_2](ClO_4)_2$
4f	4-Br-C_6H_4	CH_3	10	95	$[PhBs]ClO_4$
4g	3-MeO-C_6H_4	H	20	91	$[PipBs_2](ClO_4)_2$
4g	3-MeO-C_6H_4	H	25	89	$[PhBs]ClO_4$
4g	3-MeO-C_6H_4	H	25	91	$[PipBs_1]ClO_4$
4h	2-Me-C_6H_4	H	15	88	$[PipBs_2](ClO_4)_2$
4i	2-Cl-C_6H_4	H	10	90	$[PipBs_2](ClO_4)_2$
4i	2-Cl-C_6H_4	H	15	92	$[PhBs]ClO_4$
4i	2-Cl-C_6H_4	H	20	93	$[PipBs_1]ClO_4$
4j	4-NO_2-C_6H_4	H	6	90	$[PipBs_2](ClO_4)_2$
4j	4-NO_2-C_6H_4	H	10	93	$[PhBs]ClO_4$
4j	4-NO_2-C_6H_4	H	12	89	$[PipBs_1]ClO_4$
4k	4-OH-C_6H_4	H	10	96	$[PipBs_2](ClO_4)_2$
4k	4-OH-C_6H_4	H	10	90	$[PhBs]ClO_4$
4k	4-OH-C_6H_4	H	15	94	$[PipBs_1]ClO_4$
4l	3-Br-C_6H_4	H	10	90	$[PipBs_2](ClO_4)_2$
4l	3-Br-C_6H_4	H	15	86	$[PhBs]ClO_4$
4l	3-Br-C_6H_4	H	15	89	$[PipBs_1]ClO_4$
4m	4-Br-C_6H_4	H	10	91	$[PipBs_2](ClO_4)_2$

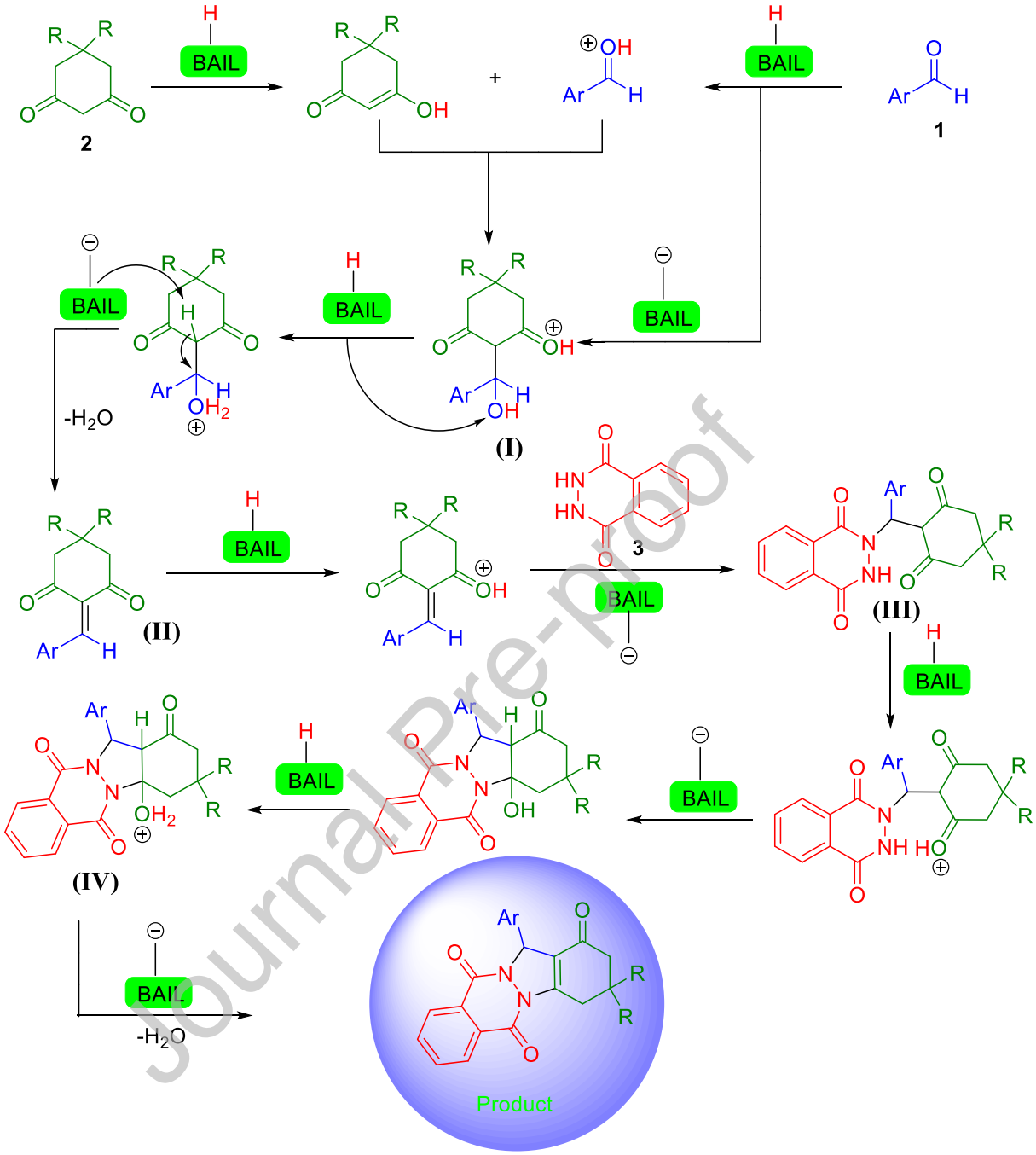
[a] Isolated Yield

In all the reactions, BAIL catalyst was simply separated and recovered. The prepared BAILs are completely soluble in H_2O and to some degree in EtOH but are not soluble in aprotic and non-polar solvents. The filtrate precipitation was recrystallized in hot EtOH to give pure desired 2*H*-indazolo[2,1-*b*]phthalazine-trione. From table 2, all the three BAIL catalysts worked very well and in a one-pot three component reaction type and gave target 2*H*-indazolo[2,1-*b*]phthalazine-triones in short and completely comparative times (6-25 min) at high to excellent yields (86-96%) in comparison with previous catalytic method reports. It can be seen that the substituent on the phenyl ring of aromatic aldehyde could affect the reaction time and/ or the yield of the product. The electron-withdrawing substituents usually lead to shorter reaction times and also increase the yield of the product. Moreover, among the three introduced BAILs, $[PipBs_2](ClO_4)_2$ catalyst showed better catalytic activity than two others catalysts and is selected as superior BAIL with respect of the optimized mol% amount of the catalyst, reaction time and yield of the obtained product.

To show the catalytic activity of the introduced BAILs, we proposed a plausible mechanism for the formation of 2*H*-indazolo[2,1-*b*]phthalazine-triones from the reaction of aromatic aldehyde (1), dimedone (2) and phthalhydrazide (3) catalyzed by BAIL catalysts. At the first, in the presence of BAIL, the carbonyl group of aromatic aldehyde (1) is activated and dimedone (2) is converted to its enol form. Then, the enol form is condensed with activated aldehyde to give intermediate (I) which after dehydration lead to form the intermediate (II). In the next step, Michel type addition reaction of phthalhydrazide (3) on the intermediate (II) followed by cyclization and dehydration in the presence of BAIL furnish the desired 2*H*-indazolo[2,1-*b*]phthalazine-trione product (4) (Scheme 6).

2.6. Reusability study

One of the most important properties for any catalyst is its simple recoverability and its ability to keep the catalytic activity over several runs. To investigate this property for introduced novel BAILs, the preparation reaction of 4a catalyzed by $[PipBs_2](ClO_4)_2$ was selected as model. After completion of the reaction, H_2O was added to the mixture and then stirred for 5 min, the reaction mixture was filtered. The H_2O solvent of the filtered mixture was evaporated under reduced pressure to give the recovered BAIL as precipitate which was washed several times with diethyl ether and n-hexane for further uses. The yield of the product was calculated after recrystallization of filtrate precipitation in hot EtOH. The results regarding the reaction times and yield of the product are graphically illustrated in Fig 6. The yield of the product was not decreased during 4 consecutive runs while the reaction time was fixed on 10 minutes. This observation means that the catalyst has been almost completely recovered and its efficiency has been retained without any decrease.



Scheme 6 The proposed mechanism for the synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones catalyzed by the introduced BAILs

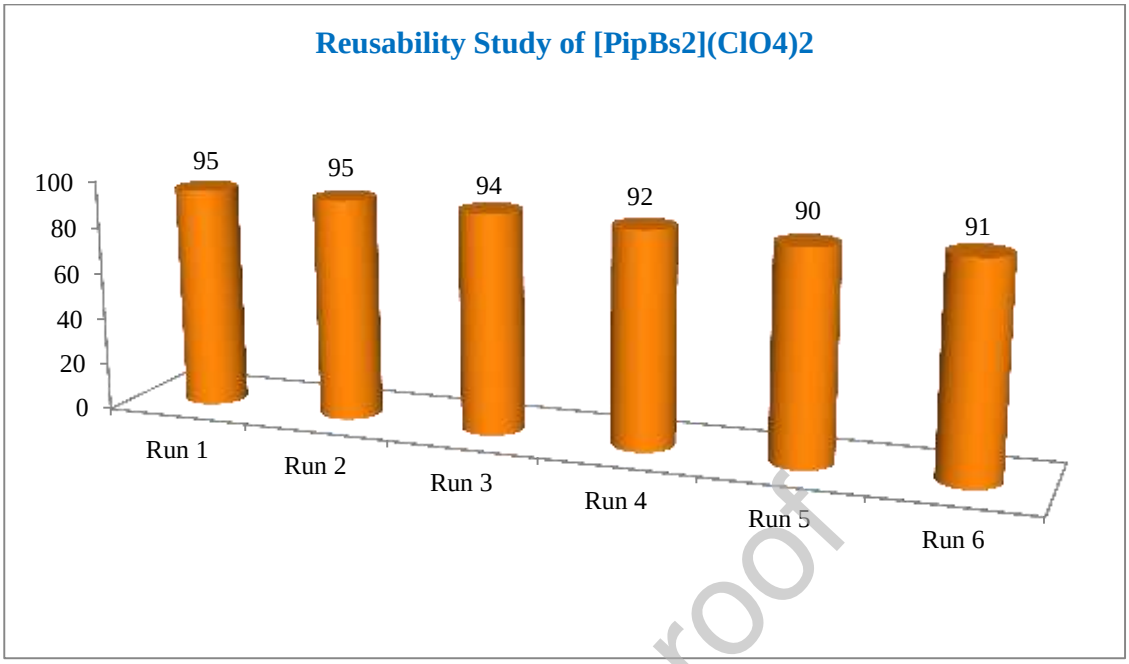


Fig. 6 Reusability study of $[PipBs_2](ClO_4)_2$ catalyst for the preparation of 4a product

3. Materials and Methods

NMR spectra were recorded at a Bruker Avance DPX 400 MHz (^{1}H) and 100 MHz (^{13}C) at 298 K using tetramethylsilane (0 ppm) as the internal reference. NMR spectroscopic data were recorded in D_2O, DMSO(d_6) and $CDCl_3$ using as internal standards the residual nondeuteriated signal for ^{1}H NMR and the deuteriated solvent signal for ^{13}C NMR spectroscopy. DEPT spectra were used for the assignment of carbon signals. Chemical shifts (δ) are given in ppm, and coupling constants (J) are given in Hertz. The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet. Melting points were collected using a capillary melting point apparatus and are uncorrected. UV-Vis spectra were recorded on Perkin-Elmer Lambda 365 UV–vis spectrophotometer at room temperature. Fourier transform infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range 400–4000 cm^{-1} using an AVATAR 370 Thermo Nicolet spectrophotometer. Elemental analyses (C, H, and N) were performed with a Heraeus CHN-O-Rapid analyzer. The thermogravimetric (TG) analysis was performed on Netsch STA449c. The sample weight was *ca.* 10 mg and was heated from room temperature up to 600˚C with 10˚C/min using alumina sample holders.

3.1. Experimental

3.1.1. Preparation of 4-(1,4-dimethylpiperazin-1-ium-1-yl)butane-1-sulfonate ($PipBs_1$)

A round bottom flask filled with 1,4-dimethylpiperazine (10 mmol) and 1,4-butane sultone (15 mmol) was allowed to stir for 4 h at room temperature under inert atmosphere (N_2 flow). The yielding white

precipitate ($PipBs_1$) was separated through filtration followed by washing with diethyl ether (3×20 mL) and then drying under vacuum. 95% yield of white solid product was obtained.

^{1}H NMR (400 MHz, D_2O, TMS): δ 1.65-1.80 (m, 2H), 1.81-1.97 (m, 2H), 2.28 (s, 3H), 2.66-2.86 (m, 4H), 2.88 (t, 3H, *J*= 6.8 Hz), 3.02 (s, 3H), 3.20-3.50 (m, 5 H). ^{13}C NMR (100 MHz, D_2O): δ 20.3, 22.1, 31.20, 46.7, 50.5, 54.0, 56.5, 58.1. Anal. Calcd for $C_{10}H_{22}N_2O_3S$: C, 47.98; H, 8.86; N, 11.19; S, 12.81. Found: 47.95; H, 8.90; N, 11.21; S, 12.83.

3.1.2. Preparation of 1,4-dimethylPiperazinium-Butane sulfonate double-linkage ($PipBs_2$)

A round-bottom flask containing a magnet was charged with 1,4-dimethylpiperazine (10 mmol) and 1,4-butane sultone (30 mmol) and stirred for 2 h under nitrogen atmosphere at 60℃. The resulting white precipitate was filtered and washed with diethyl ether and then dried in vacuum, and the resulting solid was named 1,4-dimethylPiperazinium-Butane sulfonate double-linkage ($PipBs_2$). A 90% yield of white solid product was obtained [28-30].

The spectral ^{1}H NMR, ^{13}C NMR and elemental analysis data for the 1,4-DimethylPipirazinium-Butane sulfonate double-linkage ($PipBs_2$) were as follows: ^{1}H NMR (400 MHz, D_2O, TMS): δ 1.65-1.82 (m, 4H), 1.82-2.35 (m, 4H), 2.90 (t, 4H, *J*= 8 Hz), 3.22 (s, 3H), 2.24 (s, 3H), 3.30-4.50 (m, 12H). ^{13}C NMR (100 MHz, D_2O, TMS): δ 20.2, 20.9, 22.3, 22.8, 35.7, 35.8, 47.1, 47.9, 49.7, 53.9, 54.6, 58.2, 58.8. (ESI-MS) m/z Calcd for $PipBs_2$: 386.15; Found: 306.12. Anal. Calcd for $C_{14}H_{30}N_2O_6S_2$: C, 43.50; H, 7.82; N, 7.25; S, 16.59%. Found: C, 43.40; H, 7.88; N, 7.23; S, 16.63%

3.1.3. Preparation of Phenanthrolinum-butane sulfonate ($PhBs_1$)

1,10-Phenanthroline (10 mmol) and 1,4-butane sultone (20 mmol) were dissolved in anhydrous toluene (10 mL), with a stirring at 75 °C for 48 h under nitrogen atmosphere. The resulting white precipitate (PhBS) was filtered and washed with diethyl ether and then dried in vacuum. A 87% yield of white solid product was obtained []. Anal. Calcd for $C_{16}H_{16}N_2O_3S$ (316.37): C, 60.74; H, 5.09; N, 8.86. Found: C, 60.79; H 5.1; N, 8.91%. The spectral data for Phenanthrolinum-Butane solfonate (PhBs): ^{1}H NMR (400 MHz, DMSO, TMS): δ 1.16 (quintet, 2H, *J*=7.6 Hz), 2.16 (quintet, 2H, *J*=7.6 Hz), 2.46 (t, 2H, *J*=7.6 Hz), 5.96 (t, 2H, *J*=7.6 Hz), 8.1 (m, 1H), 8.40–847 (m, 3H), 8.80-8.84 (m, 1H), 9.30-9.35 (m, 1H), 9.40-9.43 (m, 1H), 9.64-9.67 (m, 1H). ^{13}C NMR (100 MHz, DMSO): δ 22.4, 27.7, 50.7, 51.9, 56.8, 121.1, 121.3, 124.2, 128.1, 128.4, 128.8, 136.3, 138.2, 143.2, 146.9, 150.2, 199.1.

3.1.4. Preparation of $[PipBs_1]ClO_4$, $[PiPBs_2](ClO_4)_2$ and $[PhBs_1]ClO_4$

Three round-bottom flasks containing 10 ml of H_2O and a magnet were prepared and an organic salt was added to each of the flasks (20 mmol of $PhBs_1$ was added to the first flask, 20 mmol of $PipBs_1$ was added to the second flask and 10 mmol of $PipBs_2$ was added to the third flask). Then, the mixtures were stirred to obtain a homogenous solution. After that, 20 mmol of $HClO_4$ was added to each of the solutions.

Finally, the reaction mixtures were stirred at room temperature for 24 h and then the water was removed under reduced pressure. The remaining residues were dried at 50 ℃ for 4 h. At the end, $[PipBs_1]ClO_4$ $[PiPBs_2](ClO_4)_2$ and $[PhBs_1]ClO_4$ BAILs were collected with 100% yield.

3.1.5. General procedure for novel introduced BAILs catalyzed synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones

Aromatic aldehyde **1** (1 mmol), 5,5-dimethylcyclohexane-1,3-dione or cyclohexane-1,3-dione **2** (1 mmol) and 2,3-dihydro-1,4-phthalazinedione **3** (1 mmol) were placed together in a 25 mL canonical flask and an optimized amount of BAIL on the base of table 2 was added to the mixture (7 mmol% of $[PhBs_1]ClO_4$ or $[PipBs_1]ClO_4$, 3 mmol% of $[PiPBs_2](ClO_4)_2$ catalyst). The temperature was increased to 110˚C, and then the Mixture was magnetically stirred for appropriate time according to Table 3. After completion of the reaction as monitored by TLC (*n*-hexane: ethyl acetate; 3:1), the mixture was cold to room temperature and then 10 ml of H_2O was added and stirred for 5 min. The mixture was filtered and the filtrate precipitate was washed several times with hot water and then recrystallized from hot EtOH (2 × 25 mL) to provide the pure crystals of 2*H*-indazolo[2,1-*b*]phthalazine-trione derivatives. The filtered was evaporated under vacuum to precipitate the BAIL catalyst. The recovered catalyst was washed with ether, dried and stored for further similar consecutive runs. The products are known compounds and are characterized by IR and NMR spectroscopy and CHN data for new compounds. Their melting points are compared with reported values [28].

3.2. Selected spectral data

3,4-Dihydro-3,3-dimethyl-13-phenyl-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione *(4a)*

Yield: 0.37 g (97 %); M.P. = 210-212 °C; IR (KBr): $\bar{\nu}$ = 3031, 2961, 2873, 1668, 1630, 1605, 1361, 1314, 1270, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.22 (6H, s, $2CH_3$), 2.35 (2H, s, CH_2), 3.26 (1H, AB System, dd, $^2J_{HH}$ = 19.1 and $^4J_{HH}$ = 2.3 Hz, CH), 3.43 (1H, AB System, dd, $^2J_{HH}$ = 19.1 and $^4J_{HH}$ = 1.2 Hz, CH), 6.46 (1H, s, CH), 7.09-7.13 (1H, m, CH), 7.20-7.24 (1H, m, CH), 7.28-7.36 (1H, m, CH), 7.42-7.44 (2H, m, 2CH), 7.83-7.87 (2H, m, 2CH), 8.26-8.28 (1H, m, CH), 8.34-8.39 (1H, m, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.7, 29.3, 34.9, 38.1, 50.7, 65, 118.6, 127.1, 127.7, 128.2, 127.9, 128.2, 128.4, 128.7, 129.1, 133.6, 134.5, 136.4, 150.9, 154.3, 156.1, 192.2 ppm; Anal. Calcd for $C_{23}H_{20}N_2O_3$ (372.41): C, 74.17; H, 5.41; N, 7.52. Found: C, 74.22; H, 5.40; N, 7.56 %.

3,3-dimethyl-13-p-tolyl-3,4-dihydro-1*H*-indazolo[2,1-*b*]phthalazine-1,6,11(2*H*,13*H*)-trione($C_{24}H_{22}N_2O_3$, **4b**)

Yellow powder; FT- IR: (KBr) ν(cm^{-1}): 2957, 1666, 1630, 1359, 1313, 1269, 700. ^1H NMR (400 MHz, $CDCl_3$): δ 8.36-8.8 (1H, m), 8.28-8.30 (1H, m), 7.85-7.87 (2H, m), 7.29-7.34 (2H, m), 7.15-7.17 (2H, m), 6.44 (1H, s), 3.23-3.46 (2H, AB system, *J* 19.2 Hz), 2.36 (2H, s), 2.32 (3H, s), 1.23 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 156.0, 154.2, 150.7, 138.5, 134.4,133.5, 133.4, 129.4, 129.1, 129.0, 127.9, 127.7, 127.0, 118.7, 114.1, 64.8, 50.9, 38.0, 34.6, 28.7, 28.5, 21.2. Anal. Calcd. for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25; Found: C, 74.70; H, 5.70; N, 7.30.

3,4-Dihydro-3,3-dimethyl-13-(4-fluorophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11 (13*H*)-trione *(4c)*

Yield: 0.38 g (97 %); M.P. = 222-224 ^{o}C; IR (KBr): $\bar{\nu}$ = 3073, 2961, 2877, 1668, 1630, 1604, 1510, 1469, 1360, 1313, 1270, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.23 (6H, s, $2CH_3$), 2.36 (2H, s, CH_2), 3.25 (1H, AB System, dd, $^{2}J_{HH}$ = 19.1 and $^{4}J_{HH}$ = 2.3 Hz, CH), 3.43 (1H, AB System, dd, $^{2}J_{HH}$ = 19.1 and $^{4}J_{HH}$ = 1.2 Hz, CH), 6.45 (1H, s, CH), 7.03 (2H, t, $^{3}J_{HH}$ = 8.6 Hz, 2CH), 7.4-7.43 (2H, m, 2CH), 7.85-7.89 (2H, m, 2CH), 8.25-8.30 (1H, m, CH), 8.34-8.39 (1H, m, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.4, 28.7, 37.9, 38, 50.8, 64.4, 115.6, 115.9, 118.2, 127.7, 128, 128.9, 129, 132.3, 133.6, 134.6, 151, 154.4, 156, 162.7 (d, $^{1}J_{FC}$ = 264 Hz), 192.2 ppm; Anal. Calcd for $C_{23}H_{19}FN_2O_3$ (390.4): C, 70.76; H, 4.91; N, 7.18; F, 4.87. Found: C, 70.81; H, 4.88; N, 7.28; F, 4.90 %.

3,4-Dihydro-3,3-dimethyl-13-(2-chlorophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11 (13*H*)-trione *(4d 8b)*

Yield: 0.36 g (88 %); M.P. = 262-264 ^{o}C; IR (KBr): $\bar{\nu}$ = 2958, 1666, 1469, 1360, 1314, 1270, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.22 (3H, s, CH_3), 1.23 (3H, s, CH_3), 2.34 (2H, s, CH_2), 3.26 (1H, AB System, dd, $^{2}J_{HH}$ = 19.1 and $^{4}J_{HH}$ = 2.3 Hz, CH), 3.42 (1H, AB System, dd, $^{2}J_{HH}$ = 19.1 and $^{4}J_{HH}$ = 1.1 Hz, CH), 6.69 (1H, s, CH), 7.23-7.35 (3H, m, 3CH), 7.49-7.50 (1H, m, CH), 7.84-7.89 (2H, m, 2CH), 8.25-8.28 (1H, m, CH), 8.37-8.39 (1H, m, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.4, 28.8, 34.6, 38, 50.8, 64.1, 116.7, 127.7, 128, 128.7, 129.1, 129.9, 130.2, 130.5, 132.6, 133, 133.6, 134.5, 151.8, 154.2, 156.2, 192.1 ppm; Anal. Calcd for $C_{23}H_{19}ClN_2O_3$ (406.86): C, 67.89; H, 4.71; N, 6.89; Cl, 8.72. Found: C, 67.82; H, 4.76; N, 6.94; Cl, 8.68 %.

3,4-Dihydro-3,3-dimethyl-13-(4-bromophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11 (13*H*)-trione *(4f, 8i)*

Yield: 0.40 g (87 %); M.P. = 261-263 ^{o}C; IR (KBr): $\bar{\nu}$ = 2959, 1660, 1363, 1313, 1270, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.22 (3H, s, CH_3), 1.23 (3H, s, CH_3), 2.36 (2H, s, CH_2), 3.26 (1H, AB System, dd, $^{2}J_{HH}$ = 19.1 and $^{4}J_{HH}$ = 2.3 Hz, CH), 3.42 (1H, AB System, dd, $^{2}J_{HH}$ = 19.1 and $^{4}J_{HH}$ = 1.2 Hz, CH), 6.44 (1H, s, CH), 7.32 (2H, d, $^{3}J_{HH}$ = 8.6 Hz, 2CH), 7.38 (2H, d, $^{3}J_{HH}$ = 8.6 Hz, 2CH), 7.86-7.91(2H, m, 2CH), 8.28-8.3 (1H, m, CH), 8.37-8.39 (1H, m, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.5, 28.7, 34.7, 38.1, 50.9, 64.4, 118.1, 127.8, 128.1, 128.5, 128.9, 133.7, 134.5, 134.6, 134.9, 151.1, 154.4, 156, 192.1 ppm; Anal. Calcd for $C_{23}H_{19}BrN_2O_3$ (451.32): C, 61.21; H, 4.24; N, 6.21; Br, 17.71. Found: C, 61.28; H, 4.2; N, 6.18; Br, 17.65 %.

3,4-Dihydro-13-(2-chlorophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione *(4i, 8n)*

Yield: 0.32 g (83 %); M.P. = 226-228 ^{o}C; IR (KBr): $\bar{\nu}$ = 3059, 2956, 2872, 1664, 1471, 1425, 1368, 1306, 1285, 1178, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.96-2.07 (1H, m, CH), 2.23-2.39 (1H, m, CH), 2.46-2.49 (1H, m, CH), 2.52-2.67 (1H, m, CH), 3.35-3.42 (1H, m, CH), 3.51-3.57 (1H, m, CH), 6.69 (1H, s, CH), 7.06-7.52 (4H, m, 4CH), 7.86-7.88 (2H, m, 2CH), 8.26-8.28 (1H, m, CH), 8.37-8.39 (1H, m, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.3, 24.5, 36.9, 64.2, 117.7, 127.7, 128.1, 128.8, 129, 129.9, 130.2, 130.5, 132.7, 132.9, 133.3, 133.6, 134.5, 153.3, 154.2, 156.2, 192.4 ppm; Anal. Calcd for $C_{21}H_{15}ClN_2O_3$ (378.81): C, 66.60; H, 3.99; N, 7.40; Cl, 9.36. Found: C, 66.65; H, 3.94; N, 7.44; Cl, 9.31 %.

13-(4-chlorophenyl)-3,3-dimethyl-3,4-dihydro-1*H*-indazolo[2,1-*b*]phthalazine-1,6,11(2*H*,13*H*)-trione($C_{23}H_{19}ClN_2O_3$, 4e).

Yellow powder; FT- IR: (KBr) ν(cm^{-1}): 2958, 1654, 1624, 1371, 1311, 269, 697. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36-8.39 (1H, m), 8.27-8.30 (1H, m), 7.87-7.89 (2H, m), 7.29-7.34 (4H, m), 6.43 (1H, s), 3.23-3.45 (2H, AB system, *J* 19.2 Hz), 2.36 (2H, s), 1.23 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 156.0, 154.4, 151.1, 134.9, 134.6, 134.5, 133.7, 129.0, 128.9, 128.9, 128.5, 128.0, 127.7, 118.0, 64.3, 50.9, 38.0, 34.7, 28.7, 28.4. Anal. Calcd. for $C_{23}H_{19}ClN_2O_3$: C, 67.90; H, 4.71; N, 6.89; Found: C, 68.09; H, 4.65; N, 6.94.

Conclusion

Three new BAILs are introduced as task specific IL for the preparation of polycyclic 2*H*-indazolo[2,1-*b*]phthalazine-trione derivatives under solvent-free conditions at 110℃ and in all cases desired products were obtained in short times (6min-25 min) at high yields (86%-96%). These BAILs are thermally stable up to 200℃ which is reasonable and satisfactory for laboratories application. These are easy to handle powerful acidic catalysts with no corrosive properties. Hammett method and UV–vis spectroscopy were used to study their acidity and it was found that that $[PipBs_2](ClO_4)_2$ has slightly stronger acidity that $[PipBs_1]ClO_4$ and $[PhBs_1]ClO_4$ is the weakest acid among these BAILs. Moreover, the introduced BAILs are completely green and water soluble. These catalysts can be simply separated from the organic products with high recoverability/reusability ability that makes this procedure to be cost-effective and time saving method. The reusability study of the prepared BAILs showed that these task-specific ILs can be recovered and reused up to at least 6 consecutive runs without significant decrease in their efficiency. It was found that among the introduced BAILs, $[PipBs_2](ClO_4)_2$ is more superior and has better catalytic efficiency. These BAILs could be considered as green catalysts added to previously reported catalysts.

List of abbreviations

BAIL: Brønsted Acidic Ionic Liquid

$PhBs_1$: 4-(1,10-phenanthrolin-1-ium-1-yl)butane-1-sulfonate

$PipBs_1$: 4-(1,4-dimethylpiperazin-1-ium-1-yl)butane-1-sulfonate

$PipBs_2$: 1,4-dimethylpiperazine-1,4-diium-1,4-diyl)bis(butane-1-sulfonate)

BAILs-ClO_4: Brønsted acidic ionic liquids with perchlorate anion

$[PhBs_1]$-ClO_4: [4-(1,10-phenanthrolium-1-yl)butane-1-sulfonic]ClO_4^-

$[PipBs_1]ClO_4$: [4-(1,4-dimethylpiperazin-1-ium-1-yl)butane-1-sulfonic]ClO_4^-

$[PipBs_2](ClO_4)_2$: [1,4-dimethylpiperazine-1,4-diium-1,4-diyl)bis(butane-1-sulfonic)](ClO_4^-)$_2$

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Credit author statement

Fatemeh Arian: experimental

Haleh Sanaeishoar: experimental and measure the acdity function

Neda Hasanzadeh: characterization and interpretation of spectra, preparation of the manuscript draft

Mosadegh Keshavarz:

Design the work and revise the draft

Declaration of research interest

We have focused our attention on multi-component reactions specially click reaction. Moreover, we are trying to design new BAILs and solid acids using new supports. We also interested in heterogenization of organocatalysts.

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Scheme Captions

Scheme 1 Synthesis of various BAILs

Scheme 2 Preparation of novel $[PhBs_1]ClO_4$ BAIL

Scheme 3 Preparation of novel $[PipBs_1]ClO_4$ and $[PipBs_2](ClO_4)_2$ BAIL

Scheme 4 The structural configuration of new introduced BAILs

Scheme 5 Synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones catalyzed by introduced BAILs

Scheme 6 The proposed mechanism for the synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones catalyzed by the introduced BAILs

Figure Captions

Fig. 1 ^1H NMR (400 MHz, D_2O) spectrum of $PipBs_1$ (blue) and $PipBs_2$ (green)

Fig 2 FT-IR spectrum of 1,10-Phenantroline (2a) and $[PhBs_1]ClO_4$ catalyst (2b)

Fig. 3 FT-IR spectrum of 1,4-dimethyl Piperazine (3a), $[PipBs_2](ClO_4)_2$ catalyst (3b) and $[PipBs_1]ClO_4$ (3c)

Fig. 4 TGA of $[PhBs_1]ClO_4$(4a), $[PipBs_2](ClO_4)_2$ (4b) and $[PipBs_1]ClO_4$ (4c)

Fig. 5 Absorption spectra of 0.025 mg/ml 2,4-dichloro-6-nitroaniline in ethanol (a) and $[PipBs_2](ClO_4)_2$ (b).

Fig. 6 Reusability study of $[PipBs_2](ClO_4)_2$ catalyst for the preparation of 4a product

Graphical abstract